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LOW TEMPERATURE THERMAL DEGRADATION STUDIES OF STYRENE CROSS-LINKED VINYL ESTER AND POLYESTER RESINS

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Abstract

A technique for the study of low temperature (up to 400°C) thermal degradation of polymeric materials in both inert and reactive atmospheres is described. The technique utilizes a thermal desorb unit (CDS 320-011 Concentrator) coupled to a capillary gas chromatograph with mass spectrometric detection. Four styrene cross-linked thermoset resins, one vinyl ester (Derakane 510A) and three polyester (Hetron 99P, Hetron 197AT, and Vibrin F1029) resins were studied using this technique. The results indicate that the major degradation products of these resins at 300°C and 400°C result from the degradation of styrene cross-links and that the nature of the degradation products of the four resins are largely independent of the atmosphere in which the degradation takes place. At lower temperatures, i.e., 100°C and 200°C, the compounds detected appear to result from the volatilization of uncured reactants.

RÉSUMÉ

On décrit une technique permettant d'étudier la dégradation thermique à basse température (jusqu'à 400 °C) de matières polymériques en atmosphères inertes et réactives. Avec cette technique, on utilise un appareil de désorption thermique (concentrateur CDS 320-011) couplé à un chromatographe en phase gazeuse à colonne capillaire muni d'un détecteur à spectromètre de masse. On a étudié quatre résines thermodurcissables/réticulées à base de styrène, soit un ester vinylique (Derakane 510A) et trois polyesters (Hetron 99P, Hetron 197AT et Vibrin F1029). Selon les résultats, les principaux produits de dégradation à 300 °C et à 400 °C sont le résultat de la destruction de la liaison de réticulation du styrène,et la nature des produits de dégradation des quatre résines est en grande partie indépendante de l'atmosphère dans laquelle la réaction a eu lieu. À des températures plus basses, c.-à-d. à 100 °C et à 200 °C, les matières volatiles décelées sont produites, semble-t-il, par dégazage des réactifs non durcis.

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Abbreviations

amu - atomic mass unit

^{o}C - degree Centigrade

cm - centimeter

DS - data system

g - gram

GC - gas chromatograph, gas chromatography

He - helium

m - meter

mm - millimeter

mg - milligram

min - minute

mL - milliliter

MS - mass spectrometer, mass spectrometry

pyr - pyrolysis

RIC - reconstructed ion chromatogram

RT - retention time

TD - thermal desorption

µ - micrometer

µL - microliter

1.0 INTRODUCTION

The increased utilization of polymers in engineering applications can be attributed to a number of factors including improved mechanical properties, improved high temperature performance, and improved resistance to environmental degradation. Further, the high strength-to-weight ratios of many fibre reinforced polymers approach those of metallic alloys some of which are made of elements that are becoming increasingly scarce, and this also stimulates the desire to use polymeric materials. As the utilization of plastics increases, costs of plastics can be expected to decrease, and this will further add to their attractiveness for many applications.

The selection of a plastic for a particular application is influenced by a number of considerations. Where several plastics meet the required mechanical properties (i.e., tensile, compressive, and impact strengths) for a given application, the final selection of a plastic is more dependent on other factors such as resistance to environmental and chemical degradation, strength-to-weight ratio, flammability and hazardous gas production, and cost.

The performance of a polymer in a fire situation is extremely important onboard Naval vessels. Polymers are inherently more vulnerable to damage by heat and flame than most metallic materials. Under the stress of heat or flame, polymers can be expected to suffer a loss of strength which will have a severe impact on load-carrying ability. In some cases polymers may also add significantly to the fire load and will themselves burn readily. If not directly involved in the fire situation polymers may undergo thermal degradation with an accompanying release of potentially hazardous and toxic fumes which will undoubtedly have an adverse effect on crew and fire fighters.

Plastics, in the presence of heat, may breakdown by thermal and thermo-oxidative degradation mechanisms. Thermal degradation of a plastic occurs when the temperature of the plastic is sufficiently high to break primary bonds and can take place in the absence of oxygen. Thermal degradation can proceed by four mechanisms[1]: namely, depolymerization, random chain scission, cleavage of side groups which is followed by fragmentation and cyclization of the main chain, and inter-chain condensation.

Oxidative degradation occurs in the presence of oxygen and is the result of the susceptibility of the polymeric material to molecular oxygen attack. The rate of oxidative degradation is directly proportional to temperature because the production of the radicals that initiate oxidative degradation increases with

temperature. Impurities and oxygenated compounds that have been incorporated into the polymer during processing also have significant effects on the overall rate of oxidative degradation.

In an atmosphere containing oxygen, the products of the complete oxidation of a polymeric material can be predicted. For example, a polymer composed of carbon, nitrogen, and hydrogen, can be expected to produce carbon monoxide, carbon dioxide, nitrogen oxides, and water upon combustion. As carbon monoxide and carbon dioxide are both deadly in high enough concentrations, any polymeric material containing carbon can produce toxic gases upon combustion.

In many instances, polymeric materials are not completely oxidized and the nature of their degradation products cannot easily be predicted. Although some generalizations can be made concerning the thermal decomposition products of various polymers, the formulation of a plastic may involve the addition of a number of chemicals including plasticizers, pigments, flame retardants, anti-oxidants, cross-linking agents, and catalysts. Processing and/or lay-up of a plastic may require the use of organic solvents to act as thinners for the polymers. As a plastic is heated, any of the materials present in the polymer matrix may be volatilized. Knowledge of the nature of the volatiles produced by various polymers would aid in the selection of plastics that would minimize the hazards associated with their use at elevated temperatures or in a fire situation.

Degradation products of polymeric materials have been studied using a number of analytical methods including pyrolysis-gas chromatography/mass spectrometry[2] (pyr-GC/MS), pyrolysis-gas chromatography[3-5] (pyr-GC), pyrolysis/mass spectrometry[6] (pyr-MS), and thermal desorption/gas chromatography/mass spectrometry[7,8] (TD-GC/MS). This paper describes an analytical method for the identification of the volatiles produced by the thermal and thermo-oxidative degradation of polymeric materials at temperatures up to 400°C in both an inert (He) and a reactive (air) atmosphere. The method utilizes a concentrator unit coupled to a capillary GC/MS system. The concentrator includes a thermal desorption unit where the sample is heated and the degradation occurs, and traps to adsorb the degradation products. The capillary GC/MS with data system separates, detects, and facilitates identification of the volatiles produced by the plastic under study. The data obtained provides useful information on the potential hazards involved with the introduction of various plastics on Naval vessels.

2.0 EXPERIMENTAL METHOD

2.1 Equipment

2.1.1 Chemical Data Systems (CDS) 320-011 Concentrator. The Chemical Data Systems 320-011 concentrator (Chemical Data Systems Oxford, Pennsylvania) consists of two modules; namely a concentrator, where the chemistry takes place, and a control module, which is a programmable microprocessor that controls the concentrator module.

The concentrator module consists of an oven where the sample is heated, two traps to collect the volatiles produced, a valve oven containing the plumbing required to flush the volatiles from one trap to the other and subsequently into a transfer line. The transfer line acts as a heated interface between the concentrator unit and a gas chromatograph.

The oven is pulse-heated and can be programmed to attain temperatures between ambient temperature and 400°C in increments of 1°C. It has a heating rate of 300°C/minute with a maximum temperature of 400°C. The oven can be cooled at a rate of 12°C/minute using compressed air.

The traps are U-shaped, 60 cm in length, and are pulse heated. The traps can be heated from ambient temperature to 350°C at a rate of 400°C/minute. Tenax TA packing was used in both traps. Volatiles are flushed from the oven by a carrier gas and adsorbed on trap A, then back-flushed onto trap B. From trap B the volatiles are desorbed and carried into the transfer line.

The temperature of the transfer line and the valve oven are programmable from ambient to 300°C in 1°C increments. The time cycles, which include the dry time for the traps, the desorb time for the traps, the bake time, i.e., the time the traps are heated to remove heavier constituents from the Tenax TA packing, and cool-down time, are programmable with settings between 1 second and 255 hours.

The concentrator can be operated with either an inert gas, such as helium, or with a reactive gas mixture, such as air, purging the sample in the oven while it is heated. The reactive gas mixture allows oxidative degradation to take place if the material is susceptible to oxidative degradation at the particular temperature to which it is heated.

The concentrator can be operated in two mode . The first is a direct injection mode where the material to be analyzed is directly injected onto the capillary column or onto the traps. If

the injection is made directly onto the column the sample has to pass through the transfer line between the desorb unit and the GC prior to analysis. When an injection is made onto the traps, the sample must be desorbed from one trap to the other prior to transfer to the GC for analysis. This type of injection can be used to determine if the traps are working properly or if the sample is moving from the concentrator to the GC through the transfer line.

The second mode involves heating the sample to be analyzed in a desorption tube or quartz tube in the oven. The volatiles produced upon heating the sample are swept by a carrier gas to a trap where they are adsorbed on a packing. The adsorbed compounds are desorbed with heating, carried to a second trap and finally carried through the transfer line and onto the GC column for separation and subsequent identification. This second mode was used in this study.

2.1.2 CDS 320-011 Programming. The programs used to control the CDS 320-011 Concentrator during the low temperature degradation studies are shown in Table 1 (100°C, 200°C and 300°C) and Table 2 (400°C). A thermal desorb time of seven minutes was utilized for the runs at 100°C, 200°C, and 300°C, while a desorb time of ten minutes was used for the runs at 400°C in both inert and reactive atmospheres.

Table 1

Parameters used to control the CDS 320-011 Concentrator for thermal desorptions carried out at 100°C, 200°C, and 300°C in both inert and reactive atmospheres. The desorb heat (DH) shown is for the run at 300°C.

Inert			Reactive		
Function	Temp °C	Time min	Function	Temp °C	Time min
DH (desorb heat)	300	7	DH	300	7
CD (cool down)		3	CD		3
DA (dry trap A)	-	-	DA	RT	5
DB (dry trap B)	-	-	DB	RT	5
TA (heat trap A)	300	7	TA	300	7
TB (heat trap B)	300	5	TB	300	5
BA (bake trap A)	325	5	BA	325	5
BB (bake trap B)	325	5	BB	325	5
VO (valve oven)	275		VO	275	
TR (transfer line)	275		TR	275	

Table 2

Parameters used to control the CDS 320-011 concentrator for the thermal desorptions carried out at 400°C in both inert and reactive atmospheres.

Inert			Reactive		
Function	**Temp °C**	**Time min**	**Function**	**Temp °C**	**Time min**
DH (desorb heat)	400	10	DH	400	10
CD (cool down)		3	CD		3
DA (dry trap A)	-	-	DA	RT	5
DB (dry trap B)	-	-	DB	RT	5
TA (heat trap A)	300	7	TA	300	7
TB (heat trap B)	300	5	TB	300	5
BA (bake trap A)	325	10	BA	325	10
BB (bake trap b)	325	10	BB	325	10
VO (valve oven)	275		VO	275	
TR (transfer line)	275		TR	275	

The degradation products formed during the desorb cycle were adsorbed onto the Tenax packing in trap A. To remove the adsorbed materials, the trap was heated to 300°C and the volatiles were flushed onto trap B by the carrier gas (helium). When using the reactive atmosphere, a dry time was added between the thermal desorb and trap desorb step to ensure that oxygen was purged from the traps prior to heating. This was required to prevent oxidative degradation of the trap packing (Tenax TA) at higher temperatures. The trap was then heated for seven minutes in a bakeout step to remove less volatile compounds, if present, from the traps.

Trap B was then heated to 300°C to remove the adsorbed materials. The desorbed materials were then carried from trap B to the transfer line and consequently into the gas chromatograph.

The transfer line and the valve oven, i.e., the oven containing the plumbing connecting the various parts of the concentrator assembly, were heated to 275°C for all desorb runs to minimize the condensation of degradation products in the concentrator unit.

2.1.3 Capillary Gas Chromatography. The CDS 320-011 concentrator was interfaced to a Finnigan Model 9611 capillary gas chromatograph with a Finnigan MAT 5100 quadrupole mass spectrometer as a detector. A Durabond DB-1 (100% methyl

silicone bonded stationary phase) fused silica-type capillary column (0.25 mm inside diameter X 30 m long) with a 0.25 micrometer (μ) stationary phase film thickness was utilized for all separations. Helium was used as the carrier gas at a flow rate of approximately 1.5 mL/minute.

The temperature programs utilized to control the GC oven of the Finnigan 9611 gas chromatograph are shown in Table 3. For the thermal desorb runs at 100°C and 200°C, the oven was held at 40°C for 4 minutes, then ramped to 300°C at a rate of 10°/min. The temperature program took 30 minutes to complete. The temperature program for the thermal desorber runs at 300°C and 400°C was similar to that used at 100°C and 200°C, i.e., the oven was held at 35°C for 4 minutes, then ramped to 300°C at a rate of 10°/min, except that the oven was held at 300°C for 10 minutes. This temperature program took 40 minutes to complete.

Table 3

Temperature programs used to control the GC oven at a) 100°C, 200°C, and 300°C and b) 400°C.

a)

FROM TEMP °C	TO TEMP °C	RATE °C/min	TIME min	TOTAL TIME min
40	40	-	4.0	4.0
40	300	10.0	26.0	30.0

b)

40	40	-	4.0	4.0
40	300	10.0	26.0	30.0
300	300	-	10.0	40.0

2.1.4 Mass Spectrometer/Data System (MS/DS). The detection and identification of the degradation products of the plastics studied in this report were made on a Finnigan MAT 5100 quadrupole mass spectrometer with SuperIncos™ data system containing the National Bureau of Standards library of 38,791 mass spectra. The operation of a quadrupole mass spectrometer is discussed in Reference 9.

Data were acquired in the full scan mode from 25 to 475 atomic mass units (amus) using a 2 second scan time. To determine the retention time of a particular component from its scan number, multiply the scan number by 2 and divide by 60. For instance, a

compound that elutes at scan 300 has a retention time of 10 minutes.

Typical values of the instrument variables for the electron impact ionization source are shown in Table 4.

Table 4

Typical values of the parameters used to control the mass spectrometer and electron multiplier electronics.

Electron multiplier voltage	-1400 volts
Resolution low (RL)	132
Resolution high (RH)	94
Ion energy (IE)	2.51
Ion program (IP)	5.02
Extractor (EX)	2.82
Lens (L)	-134
Electrometer range	7

2.2 Materials. Four commercially available resin systems were studied. Hetron 99P and Hetron 197AT were supplied by Ashland Chemical, Derakane 510A was supplied by Dow Chemical, and Vibrin F1029 was supplied by Fibreglas Canada. All resins contained styrene to reduce the viscosity of the uncured resins and to act as a cross-linking agent during the curing process.

The four resins studied included three different types of 'polyester' resins. Derakane 510A is a bisphenol A-vinyl ester resin, Hetron 197AT is a bisphenol A-fumaric acid polyester resin, and Hetron 99P and Vibrin F1029 are isophthalic acid polyester resins.

The generalized structure of a vinyl ester resin is shown in Figure 1. It is prepared from bisphenol A, epichlorohydrin, and an unsaturated acid, for instance, 2-methyl-2-propenoic acid. Synthesis of this resin involves the reaction of bisphenol A with epichlorohydrin to form the diglycidyl ether of bisphenol A, which is then reacted with an unsaturated acid to give the vinyl ester resin. Derakane 510A is reported to be a flame retardant vinyl ester resin that contains both bisphenol A and tetrabrominated bisphenol A. The brominated bisphenol A acts as a fire retardant in this resin. Uncured Derakane 510A vinyl ester resin contains approximately 40% styrene as a viscosity reducer and cross-linking agent.

A generalized structure of a bisphenol A-fumaric acid polyester is shown in Figure 2. Bisphenol A-fumaric acid polyester resins are produced by the reaction of fumaric acid anhydride with propoxylated bisphenol A. It was reported that one source of the unsaturated diacid in Hetron 197AT is chlorendic anhydride (1,4,5,6,7,7-hexachlorobicyclo[2.2.1]heptene-2,3-dicarboxylic acid anhydride) which is the Diels-Alder adduct of hexachlorocyclopentadiene and 2-butenedioic acid anhydride and that some tetrabromobisphenol A is used in addition to bisphenol A to impart flame retardancy. The uncured resin contains approximately 40% styrene as a viscosity reducer and cross-linking agent.

Vibrin F1029 and Hetron 99P are isophthalic polyester resins. A generalized structure of an isophthalic polyester resin is shown in Figure 3. Isophthalic polyester resins are prepared from isophthalic acid (1,3-benzenedicarboxylic acid), ethylene oxide, and an unsaturated diacid, such as fumaric acid. Ethylene oxide and the isophthalic acid react to form a diol which condenses with the acid to form the polyester resin. Hetron 99P was reported to contain halogenated isophthalic acids to impart improved flame retardancy. Both of these uncured isophthalic polyester resins contain approximately 40% styrene.

A major structural difference between polyester and vinyl ester resins is the location of the sites of unsaturation in the resin molecules. The sites of unsaturation of polyester resins are located along the molecular chain and away from the ends of the molecule whereas with vinyl ester resins the sites of unsaturation are at the end of the resin molecule. The manufacturer of Derakane 510A suggests that vinyl ester resins exhibit improved chemical resistance and speed of cure as a result of the ease of approach of the cross-linking agent to the double bond and the increased reactivity of the terminal double bond. This should result in fewer unreacted double bonds and improve both chemical resistance and speed of cure of the resin.

An organic peroxide (methylethyl ketone peroxide) was used to promote the cure of the resins. Typically 5mL of methylethyl ketone peroxide was added to 454g of resin and the resulting mixture left to cure at room temperature for 24 hours. The resins were then post-cured for 45 minutes at 110^{o}C prior to analysis.

Approximately 1mg of sample was used for each thermal desorb run.

3.0 RESULTS AND DISCUSSION

3.1 Thermal Degradation in an Inert Atmosphere. The chromatographic trace of response versus retention time obtained with the GC/MS system is referred to as a reconstructed ion chromatogram (RIC). The RICs of the volatiles produced by the four resins; Derakane 510A, Hetron 99P, Hetron 197AT, and Vibrin F1029, acquired after heating them at 200°C, 300°C, 400°C in an inert atmosphere, are shown in Figures 4 through 15.

The major compound observed in the RICs of the four polyester resins, acquired following heating to 100°C and 200°C in an inert atmosphere, was styrene. Styrene is used as both a solvent to reduce viscosity and a cross-linking agent in these resins. The cured resins contain styrene cross-links between the vinyl ester or polyester portions of these resins. Calculations[10] indicate that the rate of thermal degradation of polystyrene is negligible at 100°C, and although the rate increases appreciably at 200°C, it still is very slow. The results lead to the conclusion that the styrene released by the polyesters at 100°C was primarily due to the volatilization of monomeric styrene trapped in the resin. A smaller peak with aretention time between 1.9 and 2.1 minutes was determined to be an ester which was probably an impurity in the resin materials. Some toluene, benzene, methylstyrene, and ethylbenzene were also observed in the chromatograms acquired at 200°C.

Styrene was the major product of the thermal degradation of the four resins in an inert atmosphere at 300°C and 400°C. Benzene, toluene, ethyl benzene, dimethyl benzene, and methyl styrene were other major products found in the degradation product of the four resins.

It is reported in the literature that polystyrene thermally degrades by a random chain scission mechanism[1]. Random chain scission is followed by depolymerization of the radical fragments formed to yield the monomer, styrene, and some dimer and trimer. To determine what degradation products, in addition to styrene, might be produced by the styrene cross-links, a sample of polystyrene was thermally degraded at 400°C. The RIC is shown in Figure 28. The major thermal degradation products at 400°C were benzene (scan 90), toluene (scan 144), xylene (scan 210), styrene (scan 231), and methylstyrene (scan 283), with lesser amounts of naphthalene (scan 387), isobenzofurandione (scan 435), biphenyl (scan 474), 1,1'(ethanediyl)bisbenzene or styrene dimer (scan 605).

On the basis of these products, it appears that the styrene cross-links are responsible for the majority of the compounds released from these resins when thermally degraded at

400°C.

3.2 Thermal Degradation in a Reactive Atmosphere. The RICs of the four resins; Derakane 510A, Hetron 99P, Hetron 197AT, and Vibrin F1029, after heating in a reactive atmosphere at 200°C, 300°C, and 400°C, are shown in Figures 16 through 27 respectively.

The rate of oxidative degradation is also directly related to the temperature to which the sample is exposed. As oxygen is present during the degradation, the structures and relative concentrations of the degradation products might be expected to vary from those found when an inert atmosphere is used.

There was, however, little difference between the degradation products of the four resins when degraded in a reactive atmosphere as opposed to an inert atmosphere. Styrene was the major degradation product of the four resins at 100°C, 200°C, 300°C, and 400°C. However, there was an increase in the relative intensity of the peak corresponding to benzaldehyde for the runs at 300°C and 400°C in a reactive atmosphere as compared to those in an inert atmosphere.

3.3 Thermal Degradation of the Ester Portion of the Resins. In order to determine degradation products that were characteristic of the polyester and vinyl ester portions of the four resins, styrene was separated from the ester portion of the uncured resins by preparative thin layer chromatography (TLC) and the esters were thermally degraded at 400°C.

The RIC of Derakane 510A vinyl ester (no styrene) is shown in Figure 29. The major degradation products of the vinyl ester portion of Derakane 510A resin were phenol (scan 283), benzene (scan 93), toluene (scan 148), and isobenzofurandione (scan 432). Other compounds detected that were characteristic of a vinyl ester resin containing tetrabrominated bisphenol A were 2-methylpropenoic acid (scan 207), bromobenzene (scan 250), bromophenol (scan 328), 4-methylphenol (scan 335), 2-methylbenzofuran (scan 348), and 4-(1-methylethyl)phenol (scan 408). This is in contrast to the the major degradation products of the styrene cross-linked (cured) resin where the major products, i.e., styrene, benzene, toluene, methylstyrene, and xylene, were similar to those produced by a sample of polystyrene.

The presence of brominated benzenes and phenols in the chromatogram indicate that the bisphenol A part of the resin was partially halogenated. Halogenation of resins is a common way of

introducing flame retardancy. Halogens are thought to interfere with the free radical propagation of the thermal degradation of a material, thus reducing the rate of the reactions that produce flammable volatiles.

The RIC of Vibrin F1029 resin after the styrene had been removed is shown in Figure 30. The major degradation products were benzene (scan 93), 1,3-isobenzofurandione (scan 433), and toluene (scan 147). Some styrene (scan 226) was observed and may have resulted from an incomplete removal of the styrene from the polyester portion of the resin during the separation step or from the reaction of styrene with the resin.

The RIC of Hetron 197AT polyester after the styrene had been removed is shown in Figure 31. The major thermal degradation products of the polyester portion of Hetron 197AT were benzene (scan 94), toluene (scan 148), 1,3,5-trichlorobenzene (scan 382), xylene (scan 216), ethylbenzene (scan 210), chlorobenzene (scan 195), and 1,3-isobenzofurandione (scan 432). Some styrene was observed and probably resulted from incomplete separation of components of the resin. A number of halogenated aromatics, in addition to triclorobenzene, were also found during analysis of the degradation products. These included bromobenzene (scan 250), 4-bromo-1,2-dichlorobenzene (scan 424), 1,3-dibromo-5-chlorobenzene (scan 467), and 1,3,5-tribromobenzene (scan 507). Hetron 197AT was reported to be a bisphenol A-fumaric acid polyester flame retardant resin containing HET and some tetrabrominated bisphenol A. The presence of halogenated aromatics indicates that the polyester portion of the resin contained a source of halides, for example, HET or halogenated phthalic acids. No phenol or substituted phenols, which would suggest the presence of bisphenol A or tetrabrominated bisphenol A, were found in the degradation products.

The RIC of the ester portion of Hetron 99P polyester resin is shown in Figure 32. The major degradation products are benzene (scan 93), styrene (scan 226), and toluene (scan 146). The presence of styrene in the RIC may indicate that the separation of the polyester and the styrene by TLC was incomplete or that the resin has reacted with some styrene. Other degradation products found were chlorobenzene (scan 195), ethylbenzene (scan 208), dimethylbenzene (scan 214), bromobenzene (scan 249), methylstyrene (scan 282), 1-bromo-3-chlorobenzene (scan 354), 1,3,5-trichlorobenzene (scan 383), 4-bromo-,1,3-dichlorobenzene, isobenzofurandione (scan 433), and dibromochlorobenzene (scans 467, 483). The brominated and chlorinated benzenes arise from the degradation of the halogenated phthalic acids used to impart a degree of flame retardancy to this resin. Isobenzofurandione is the anhydride of isophthalic acid and is a characteristic degradation product of phthalic acid based polyester resins.

3.4 Toxicity of Degradation Products. A number of toxic and/or hazardous gases were produced by the four thermoset resins studied in this work. The most abundant product from the thermal degradation of these resins (on the basis of the intensity of the response in the RIC) was styrene. Styrene is a lachrymator and causes violent itching of and severe injury to the eyes. It is not considered to be a very toxic material under normal conditions because of its low volatility. However, at higher temperatures its volatility increases and its threat to life increases proportionately[11].

Methylstyrene is listed as an irritant[11] at lower concentrations but its toxicity increases as the concentration increases.

Benzene and toluene were also common degradation products of the polyester resins studied. Exposure to high concentrations of benzene can result in acute poisoning resulting from the narcotic action of benzene on the CNS[11]. Acute poisoning is less common from exposure to toluene. However, impairment of coordination often results and the time for this to occur decreases with an increase in toluene concentration[11].

Burning of polystyrene and styrene cross-linked resins are reported[12] to produce high levels of smoke through the release of aromatic compounds which lead to the formation of soot particles by way of the formation of polycyclic aromatic compounds. As such the aromatic degradation products (styrene, benzene, toluene, and methylstyrene) discussed above present a hazard as the precursors to the production of smoke in a fire situation.

4.0 CONCLUSIONS

An analytical technique to study the thermal degradation of polymeric materials through the analysis of degradation products has been described. Thermal degradation of polymeric materials can be studied in both inert and reactive atmospheres at temperatures up to 400°C.

The technique has been used to study the thermal degradation of four styrene cross-linked thermoset resins; a vinyl ester resin and three polyester resins. The major degradation products of each of the four resins studied were similar to those found when polystyrene was degraded, i.e., styrene, benzene, toluene, and methylstyrene, which indicates that the styrene

cross-links were the source of the majority of the degradation products produced by these resins. As a result of the toxicity of the degradation products and the role of these aromatic compounds as smoke producers, styrene cross-linked resins are poor materials for use in areas where flammability and smoke production are of concern.

VINYL ESTER

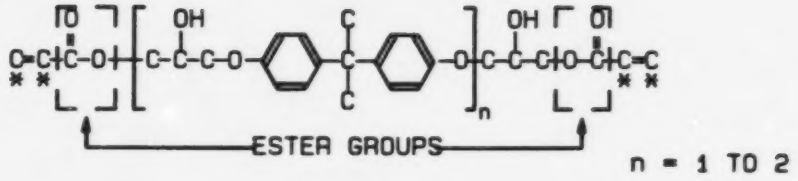

FIGURE 1: Structure of a typical bisphenol A vinyl ester.

BISPHENOL A-FUMARIC ACID POLYESTER

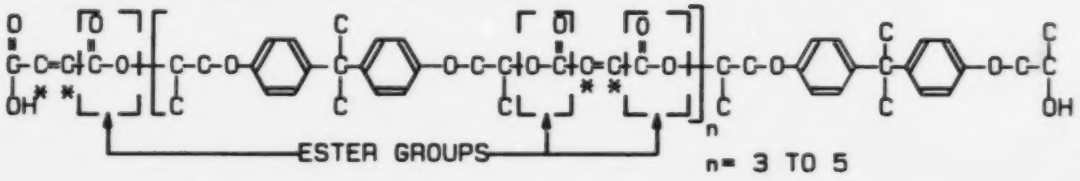

FIGURE 2: Structure of a typical bisphenol A fumaric acid polyester.

ISOPHTHALIC POLYESTER

FIGURE 3: Structure of a typical isophthalic acid polyester.

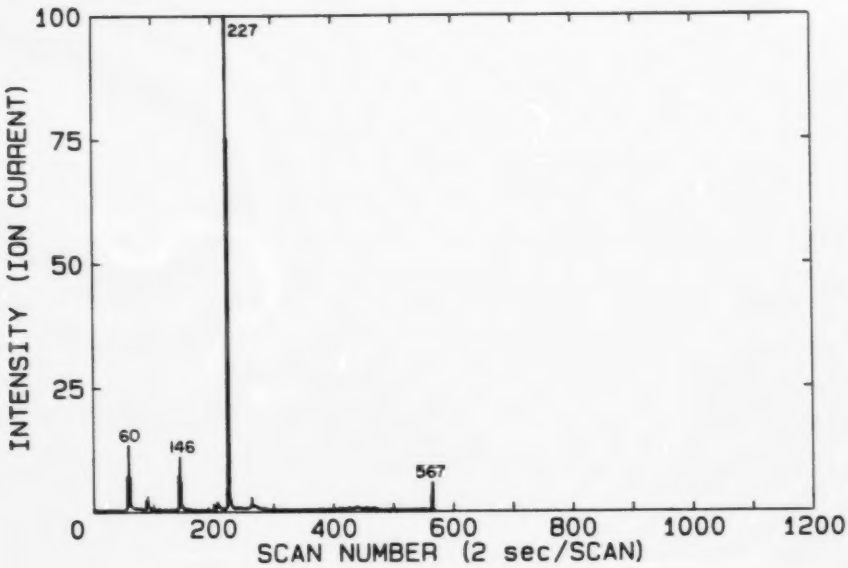

FIGURE 4: **RIC showing the compounds released from Derakane 510A resin after heating for 7 minutes at 200 C in an inert atmosphere.**

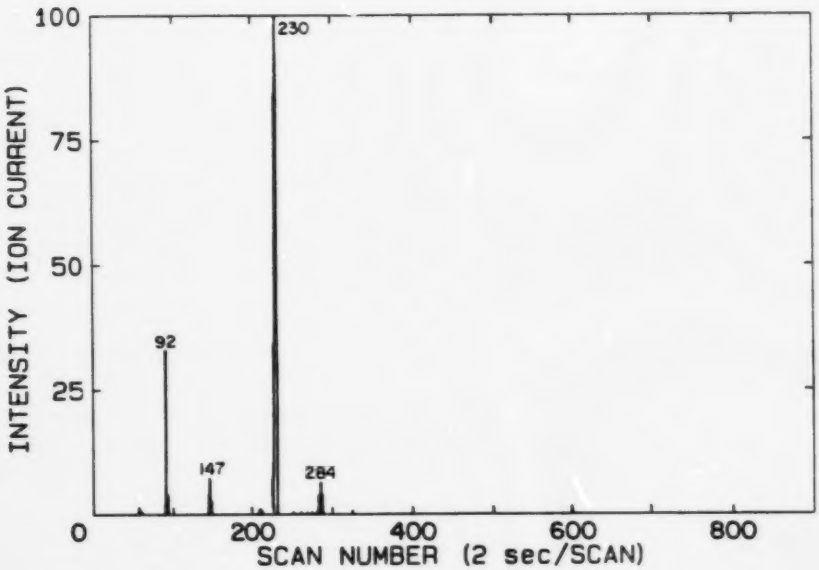

FIGURE 5: **RIC showing the compounds released from Derakane 510A resin after heating for 7 minutes at 300 C in an inert atmosphere.**

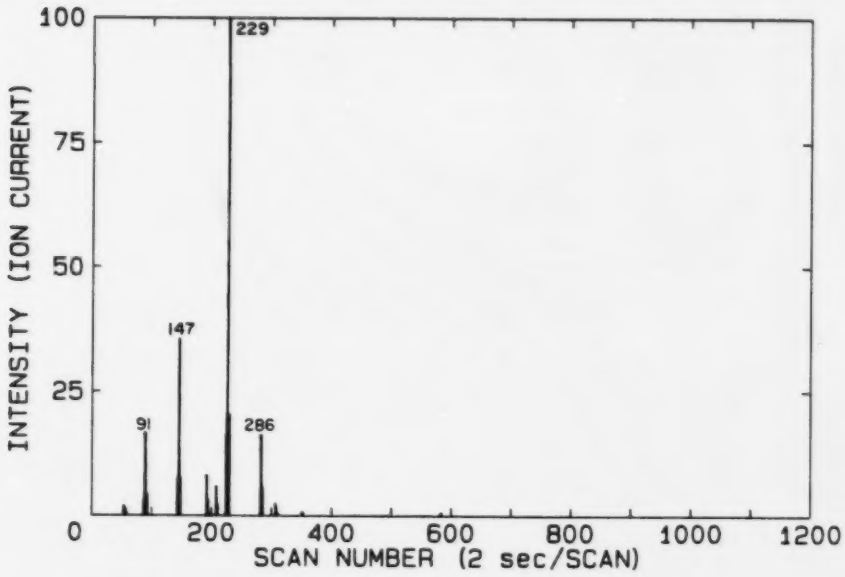

FIGURE 6: **RIC showing the compounds released from Derakane 510A resin after heating for 7 minutes at 400 C in an inert atmosphere.**

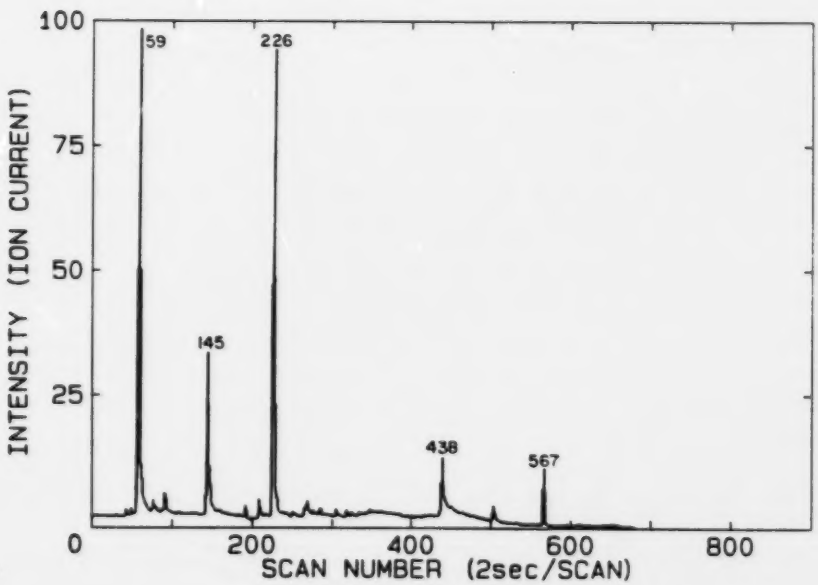

FIGURE 7: **RIC showing the compounds released from Vibrin F1029 resin after heating for 7 minutes at 200 C in an inert atmosphere.**

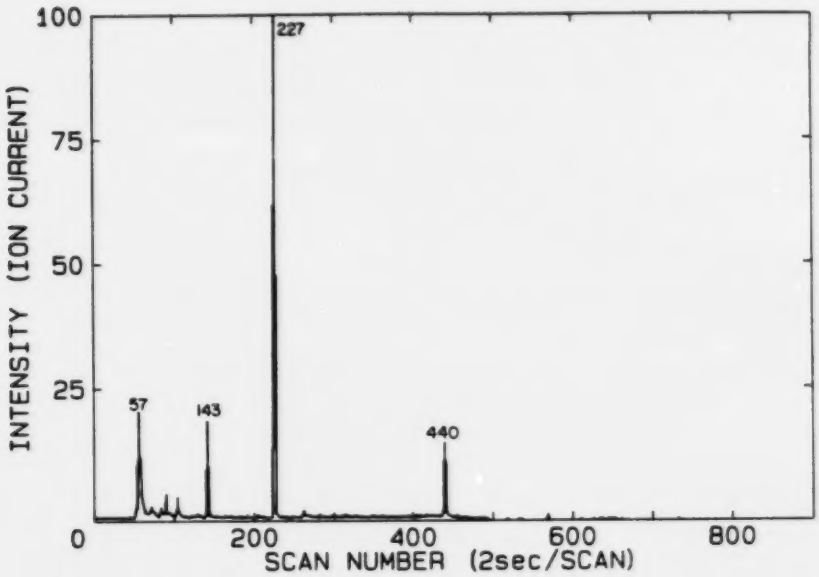

FIGURE 8: RIC showing the compounds released from Vibrin F1029 resin after heating for 7 minutes at 300 C in an inert atmosphere.

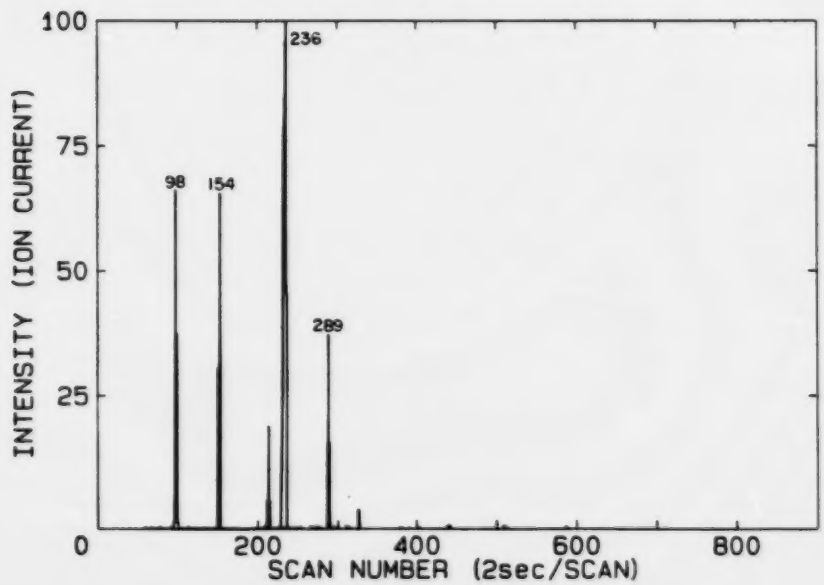

FIGURE 9: RIC showing the compounds released from Vibrin F1029 resin after heating for 7 minutes at 400°C in an inert atmosphere.

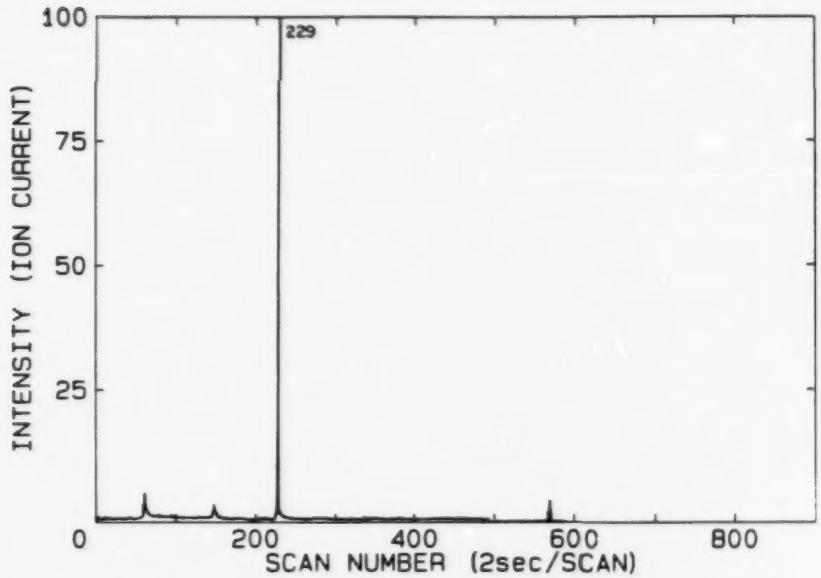

FIGURE 10: **RIC showing the compounds released from Hetron 197AT resin after heating for 7 minutes at 200°C in an inert atmosphere.**

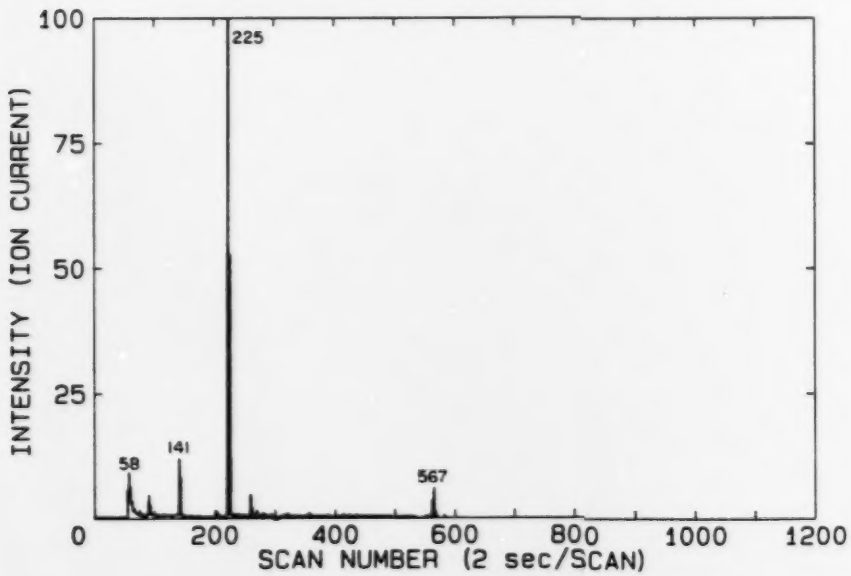

FIGURE 11: **RIC showing the compounds released from Hetron 197AT resin after heating for 7 minutes at 300°C in an inert atmosphere.**

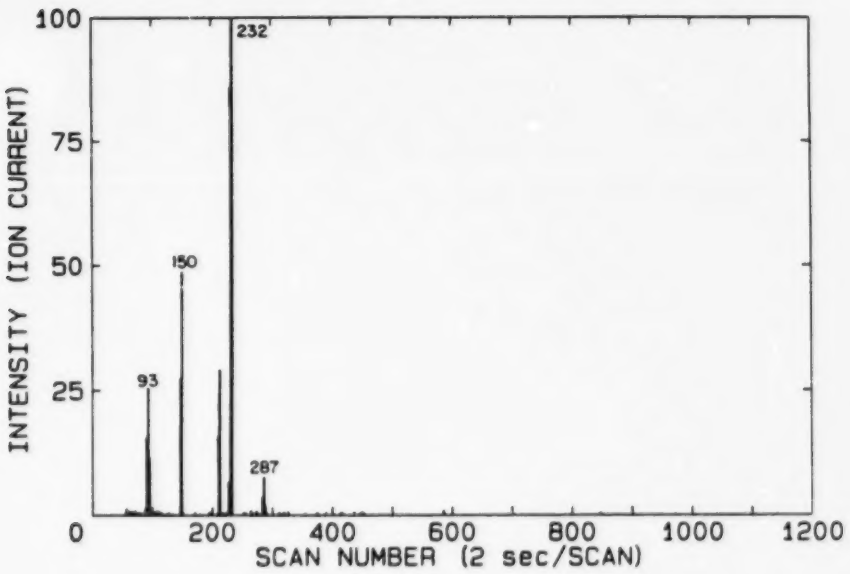

FIGURE 12: RIC showing the compounds released from Hetron 197AT resin after heating for 7 minutes at 400°C in an inert atmosphere.

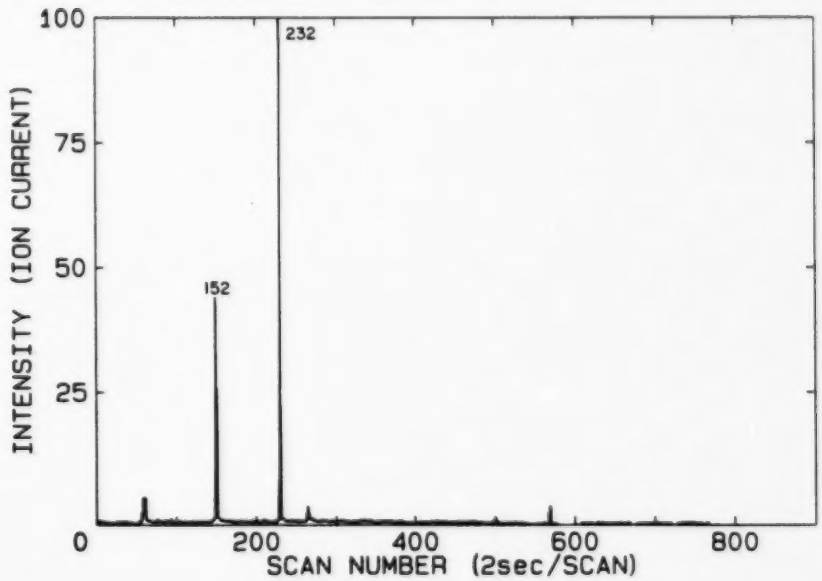

FIGURE 13: RIC showing the compounds released from Hetron 99P resin after heating for 7 minutes at 200°C in an inert atmosphere.

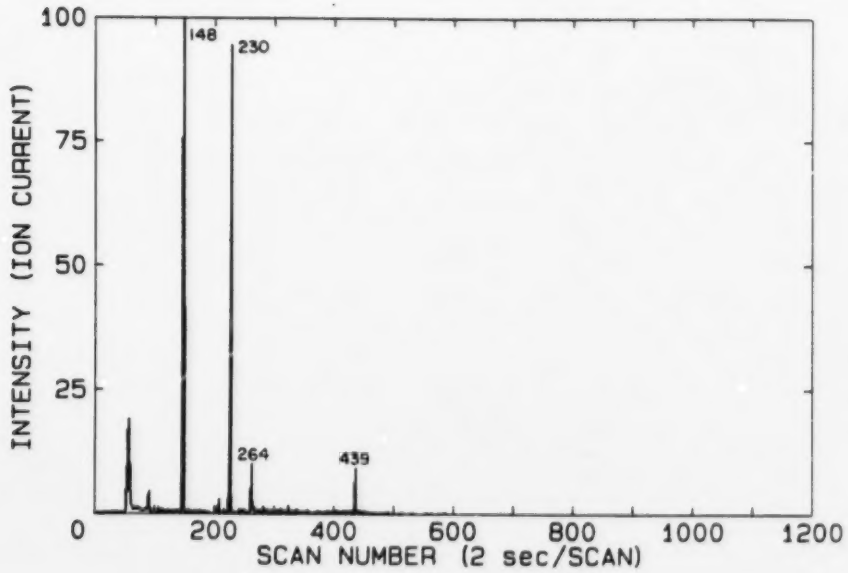

FIGURE 14: RIC showing the compounds released from Hetron 99P resin after heating for 7 minutes at 300°C in an inert atmosphere.

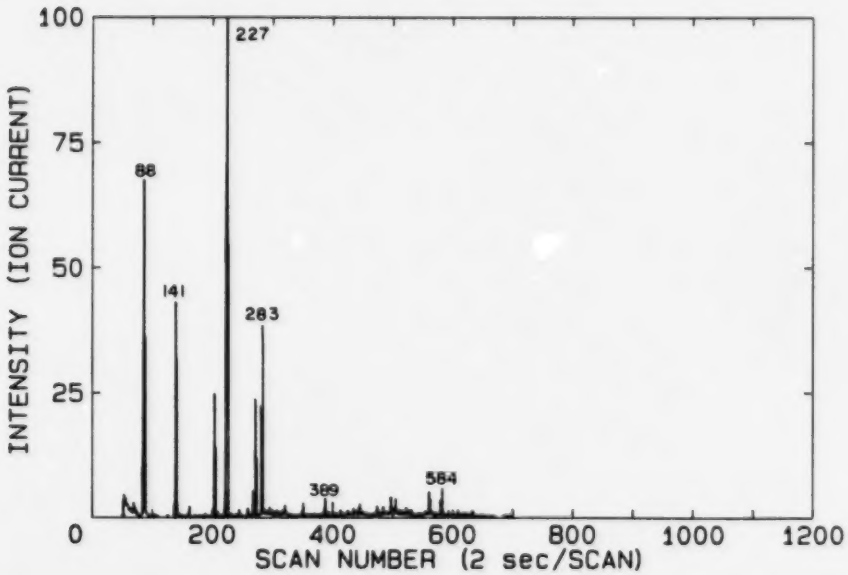

FIGURE 15: RIC showing the compounds released from Hetron 99P resin after heating for 7 minutes at 400°C in an inert atmosphere.

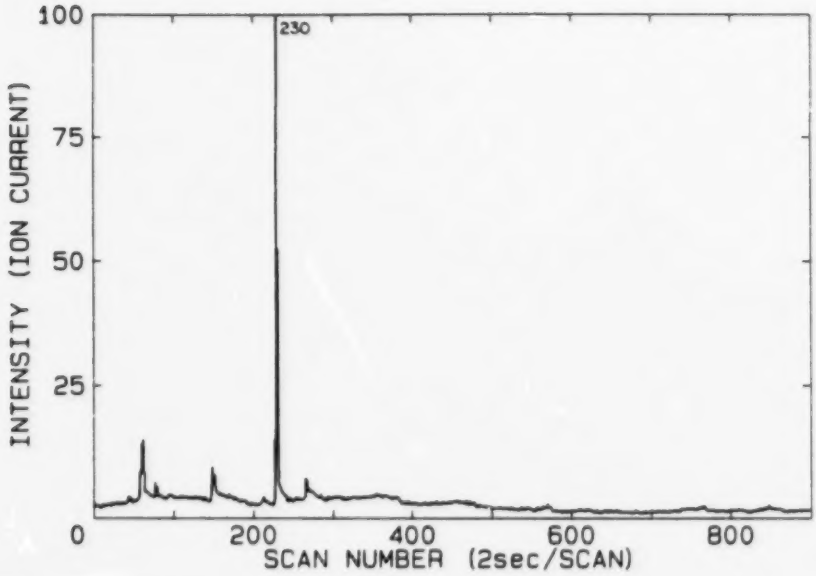

FIGURE 16: RIC showing the compounds released from Derakane 510A resin after heating for 7 minutes at 200°C in a reactive atmosphere.

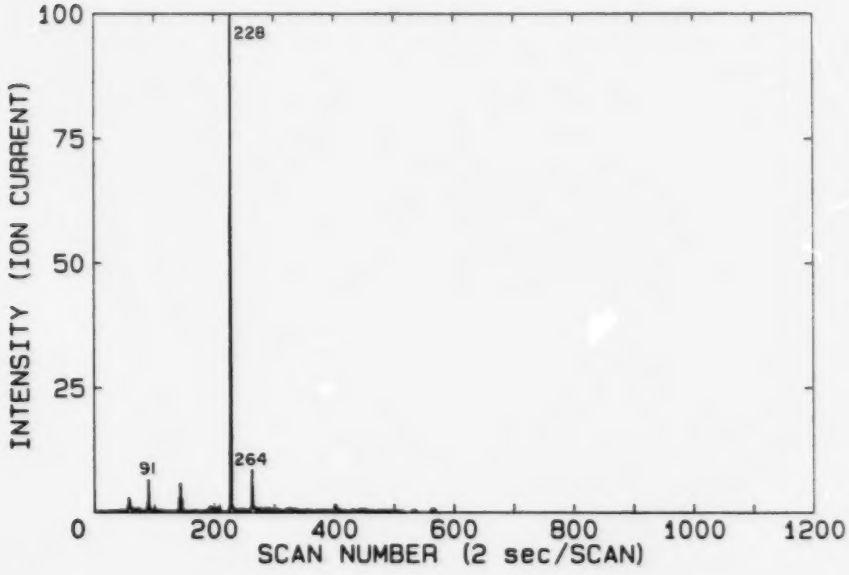

FIGURE 17: RIC showing the compounds released from Derakane 510A resin after heating for 7 minutes at 300°C in a reactive atmosphere.

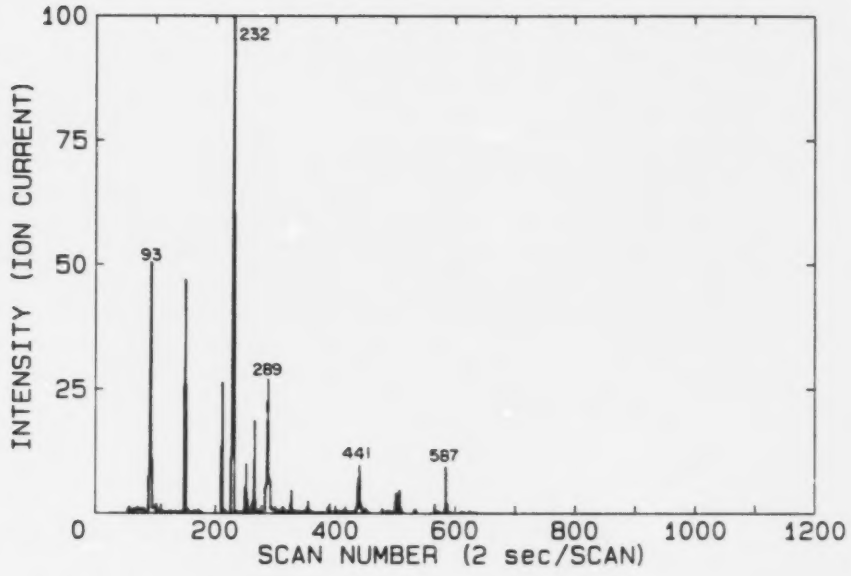

FIGURE 18: RIC showing the compounds released from Derakane 510A resin after heating for 7 minutes at 400°C in a reactive atmosphere.

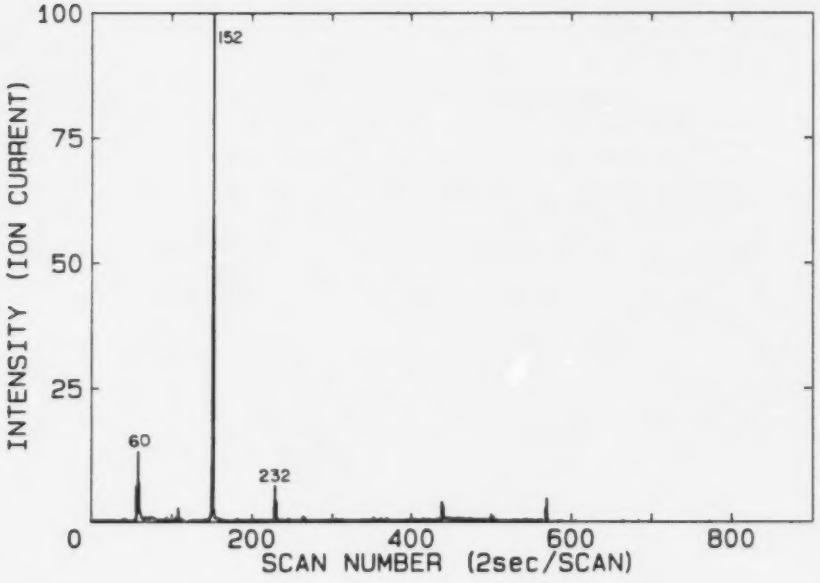

FIGURE 19: RIC showing the compounds released from Vibrin F1029 resin after heating for 7 minutes at 200°C in a reactive atmosphere.

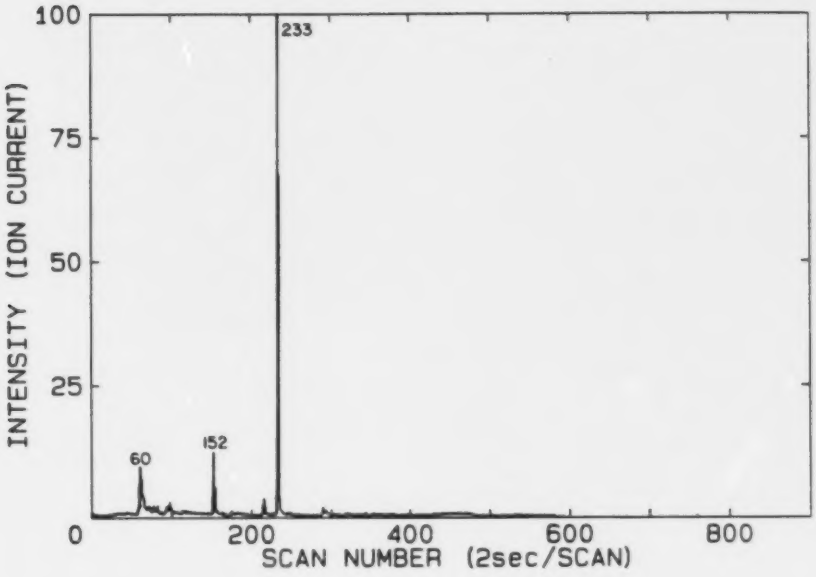

FIGURE 20: RIC showing the compounds released from Vibrin F1029 resin after heating for 7 minutes at 300°C in a reactive atmosphere.

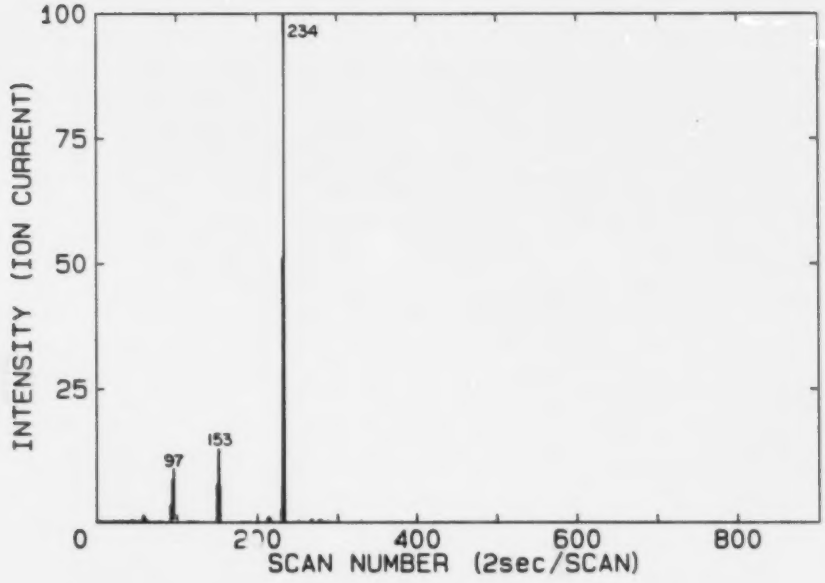

FIGURE 21: RIC showing the compounds released from Vibrin F1029 resin after heating for 7 minutes at 400°C in a reactive atmosphere.

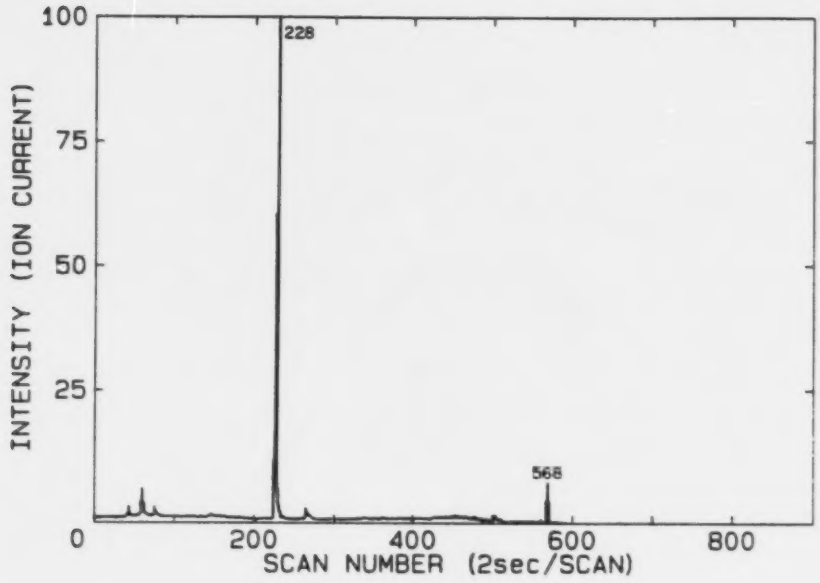

FIGURE 22: RIC showing the compounds released from Hetron 197AT resin after heating for 7 minutes at 200°C in a reactive atmosphere.

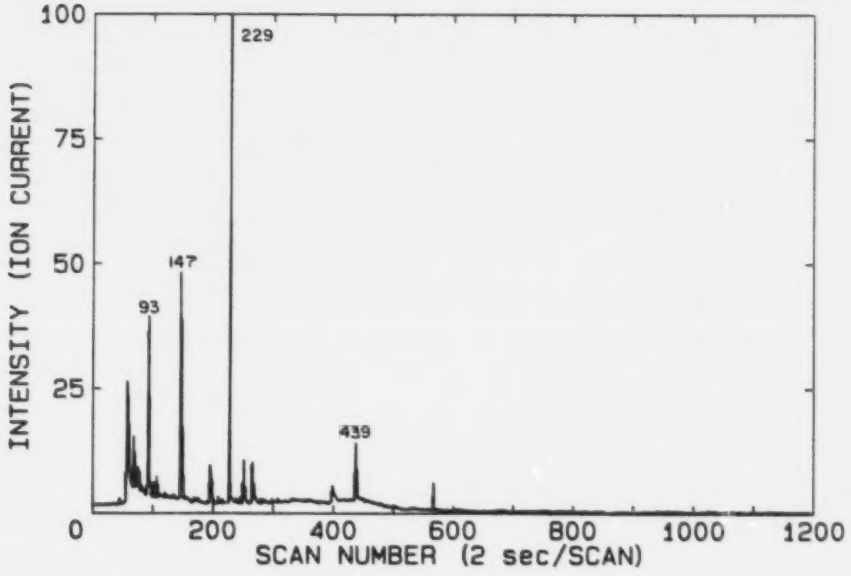

FIGURE 23: RIC showing the compounds released from Hetron 197AT resin after heating for 7 minutes at 300°C in a reactive atmosphere.

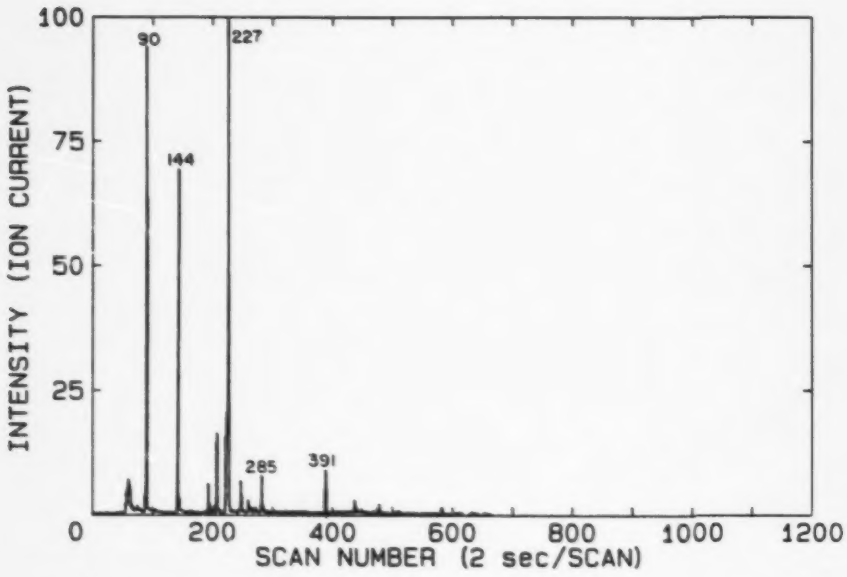

FIGURE 24: RIC showing the compounds released from Hetron 197AT resin after heating for 7 minutes at 400°C in a reactive atmosphere.

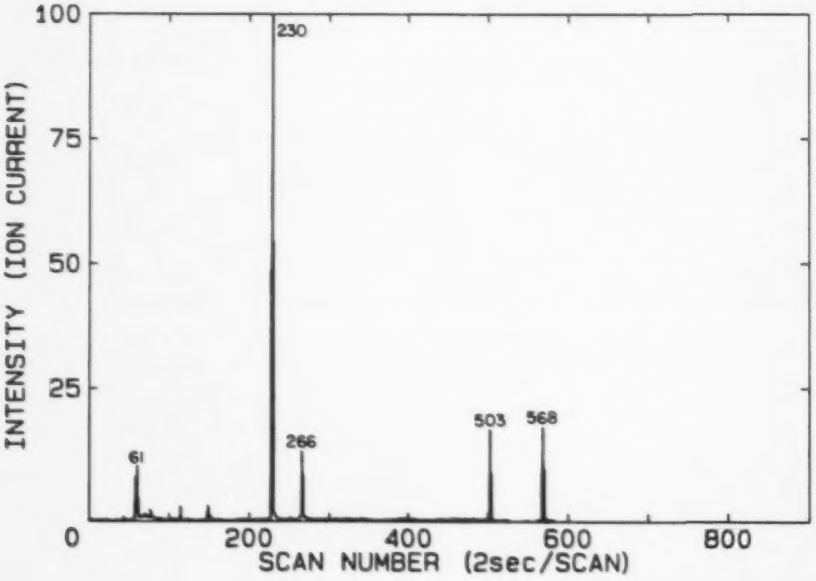

FIGURE 25: RIC showing the compounds released from Hetron 99P resin after heating for 7 minutes at 200°C in a reactive atmosphere.

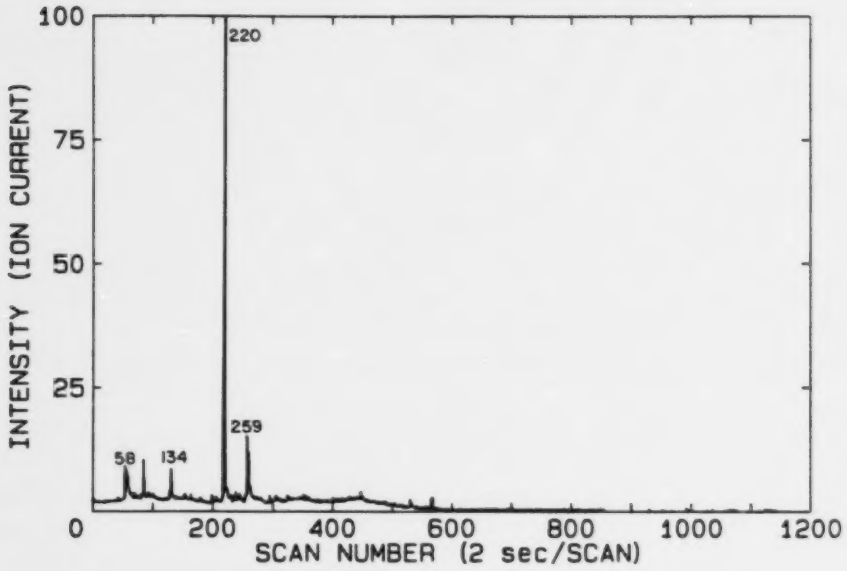

FIGURE 26: **RIC showing the compounds released from Hetron 99P resin after heating for 7 minutes at 300°C in a reactive atmosphere.**

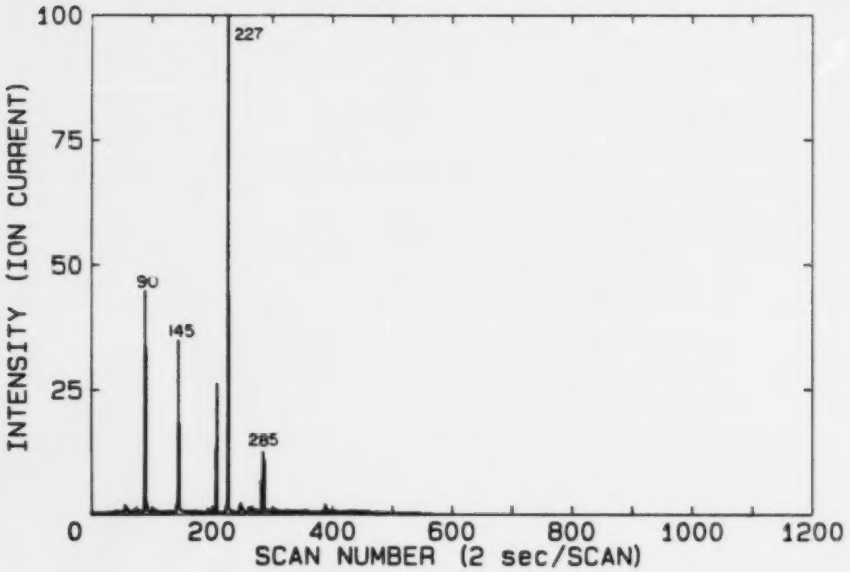

FIGURE 27: **RIC showing the compounds released from Hetron 99P resin after heating for 7 minutes at 400°C in a reactive atmosphere.**

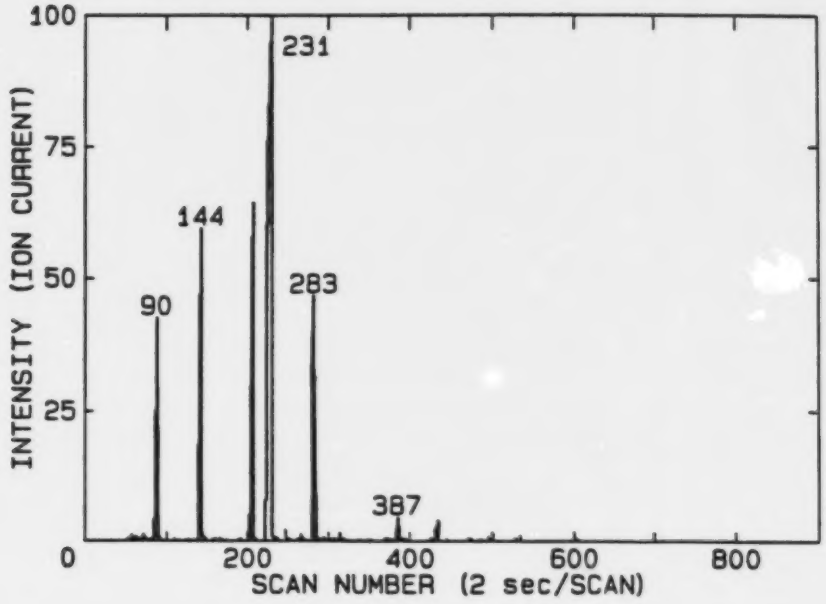

FIGURE 28: RIC showing the compounds released from a sample of polystyrene heated at 400°C for 10 minutes in an inert atmosphere.

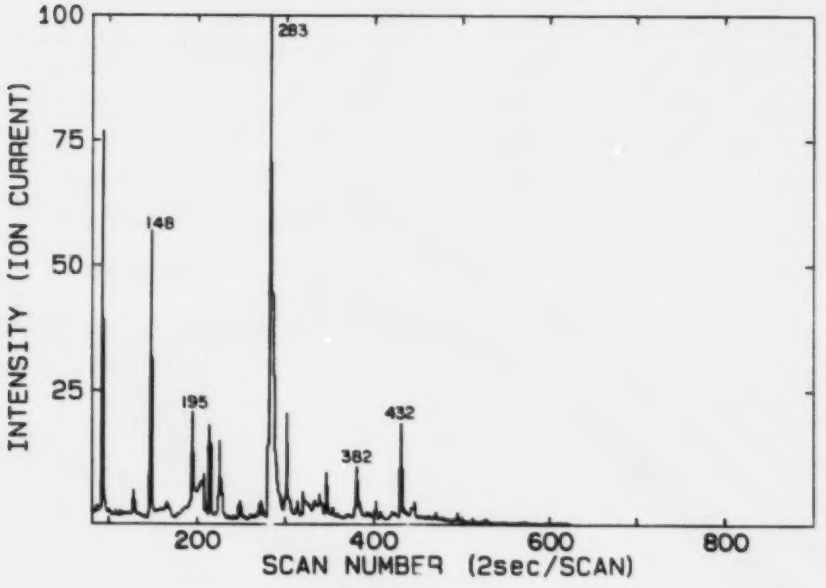

FIGURE 29: RIC showing the compounds released from the vinyl ester portion of Derakane 510A resin after heating at 400°C for 10 minutes in an inert atmosphere.

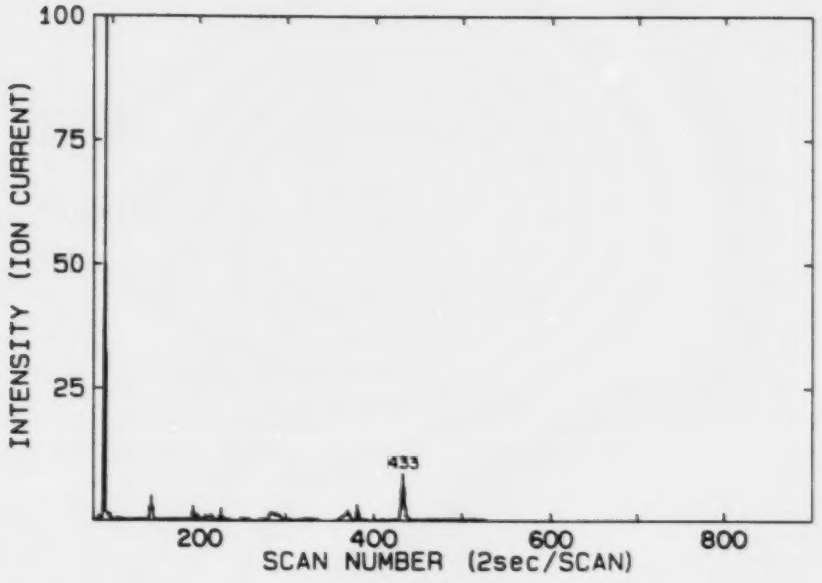

FIGURE 30: **RIC showing the compounds released from the polyester portion of Vibrin F1029 resin after heating at 400°C for 10 minutes in an inert atmosphere.**

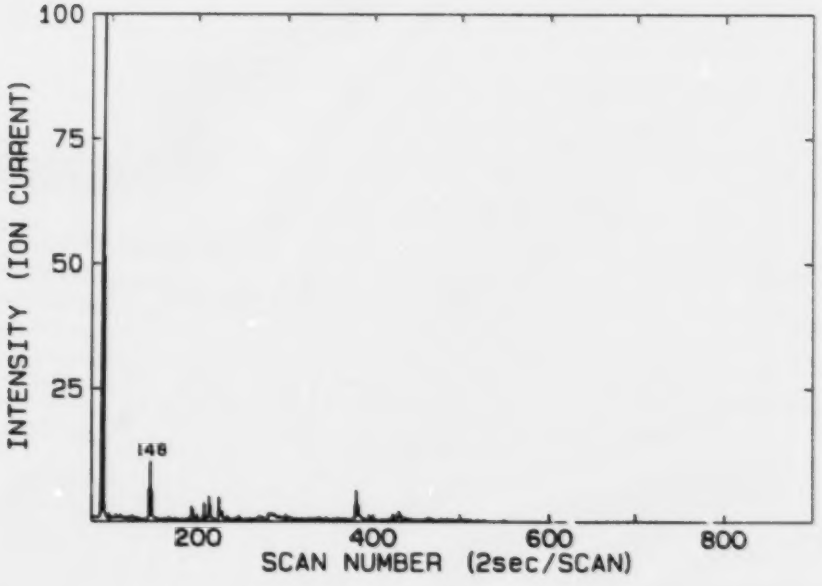

FIGURE 31: **RIC showing the compounds released from the polyester portion of Hetron 197AT resin after heating at 400°C for 10 minutes in an inert atmosphere.**

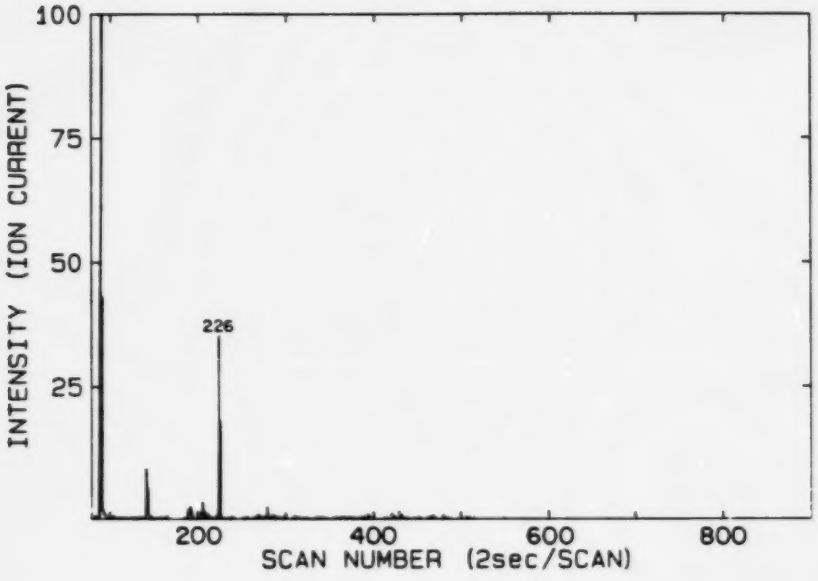

FIGURE 32: **RIC showing the compounds released from the polyester portion of Hetron 99P resin after heating at 400°C for 10 minutes in an inert atmosphere.**

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A technique for the study of low temperature (up to 400°C) thermal degradation of polymeric materials in both inert and reactive atmospheres is described. The technique utilizes a thermal desorb unit (CDS 320-011 Concentrator) coupled to a capillary gas chromatograph with mass spectrometric detection. Four styrene cross-linked thermoset resins, one vinyl ester (Derakane 510A) and three polyester (Hetron 99P, Hetron 197AT, and Vibrin F1029) resins were studied using this technique. The results indicate that the major degradation products of these resins at 300°C and 400°C result from the degradation of styrene cross-links and that the nature of the degradation products of the four resins are largely independent of the atmosphere in which the degradation takes place. At lower temperatures; i.e., 100°C and 200°C, the volatiles detected appear to result from the off-gassing of uncured reactants.

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